

Dye-sensitized Photocatalyst for Water Splitting into H₂ and O₂ Under Visible Light Irradiation

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Photocatalytic water splitting into H₂ and O₂ using semiconductors has received much attention for the potential application to direct production of H₂ as clean and high-energy resources. However, no satisfactory system workable under visible light irradiation has yet been established. As one of the strategies for an effective visible light harvest, spectra sensitization of wide bandgap semiconductors by dye molecules has so far been a subject for the investigation of photocatalytic H₂ production from water. However, most of dye molecules can not oxidize water to O₂, and decompose in the absence of sacrificial electron donor. We have recently demonstrated a new type of photocatalytic water splitting system in which H₂ production and O₂ production processes are combined with an IO₃⁻/I⁻ (or I₃⁻/I⁻) shuttle redox mediator [1,2], as shown in Fig.1. In this system the water oxidation into O₂, the most difficult process, takes place with the reduction of IO₃⁻ (or I₃⁻) to I⁻ over WO₃ photocatalyst under visible light irradiation. Therefore, a dye-sensitized photocatalyst is applicable to the H₂ production process, if it can oxidize I⁻ to I₃⁻ accompanied with H₂ production. From this viewpoint, we investigated the H₂ production from water over dye-sensitized Pt/TiO₂ photocatalysts using iodide (I⁻) as an electron donor.

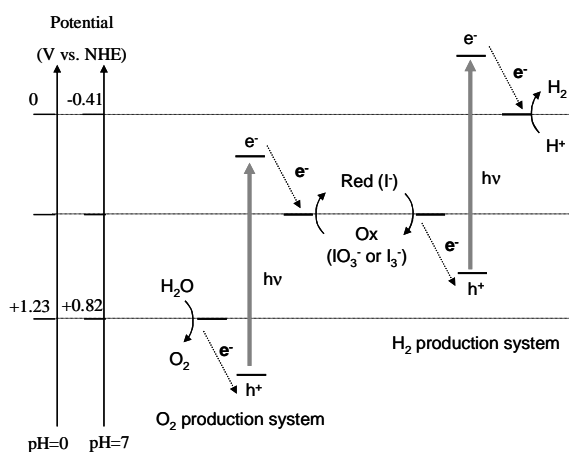


Fig. 1 Conceptual scheme of two-step water splitting.

We prepared dye-adsorbed Pt/TiO₂ (0.5 wt% of Pt loaded, anatase, 320 m²/g, Ishihara Co. Ltd. ST-01) photocatalysts and investigated H₂ evolution from water-acetonitrile mixed solutions containing NaI (0.1 M) as electron donor under visible light irradiation ($\lambda > 410$ nm). Figure 2 shows the rates of H₂ evolution over M-Pt/TiO₂ (merocyanine NK2045) N3-Pt/TiO₂ (Ru complex N3) and C-Pt/TiO₂ (coumarine C343) photocatalysts in the water-acetonitrile mixed solutions with different ratios of water to AN (5 ~ 100 %; by volume). In all cases, the rate of H₂ evolution from the water-AN mixture (water 5 %) was higher than that from the water. Especially, the rates of H₂ evolution over M-Pt/TiO₂ and N3-Pt/TiO₂ from water-AN mixture (water 5 %) were about 20 and 100 times higher than that from water, respectively. The rates of H₂ evolution over the M-Pt/TiO₂ and N3-Pt/TiO₂ were significantly decreased with the increase of water

ratio, and the rates were quite low in the range of water ratio over 50 % and 70 %, respectively. On the other hand, the influence of the water ratio to AN on H₂ evolution rate was not so marked over the C-Pt/TiO₂ and a relatively high rate of H₂ evolution was observed even in the 100% of water.

The oxidation potentials of the I₃⁻/I⁻ and dyes are plotted as a function of the water ratio in Fig. 3, in which the redox potential of the ferricenium ion ferrocene (Fc⁺/Fc) are used as a standard redox. It is clear that the oxidation potential of the I₃⁻/I⁻ redox shifted positively with the increase of water ratio to AN, while those of the dyes slightly changed. The shifts of I₃⁻/I⁻ redox causes a decrease in the energy gap (ΔG) between the I₃⁻/I⁻ redox and the HOMO level of dyes with the increase of water ratio. Because the merocyanine dye (NK2045) possesses the most negative HOMO level among the three dyes, the ΔG became quite small with the increase of water ratio, and finally became 0 V at the water ratio around 70 %. The small ΔG is certainly responsible for the low H₂ evolution rate over the M-Pt/TiO₂ photocatalyst in a water-rich solution. On the other hand, the ΔG between the I₃⁻/I⁻ and the HOMO level of the coumarin (C343) is larger enough than the value generally required for the electron transfer from I⁻ to oxidized dye, because the HOMO level is the most positive among the three dyes. Consequently, the decrease in H₂ evolution rate with the increase of water ratio was not remarkable over C-Pt/TiO₂ and a relatively high rate of H₂ evolution was observed even in water (water 100 %) as shown in Fig. 2.

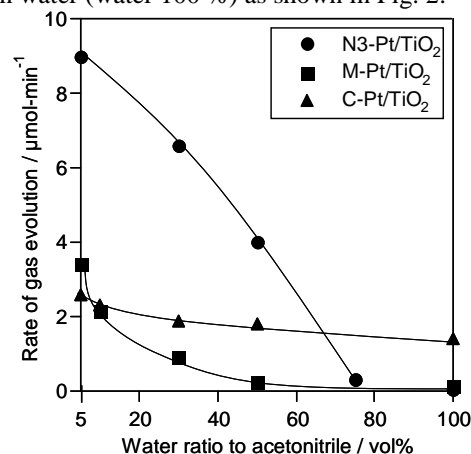


Fig. 2 Rates of H₂ evolution from mixtures with different ratios of water to acetonitrile including 0.1 M of NaI.

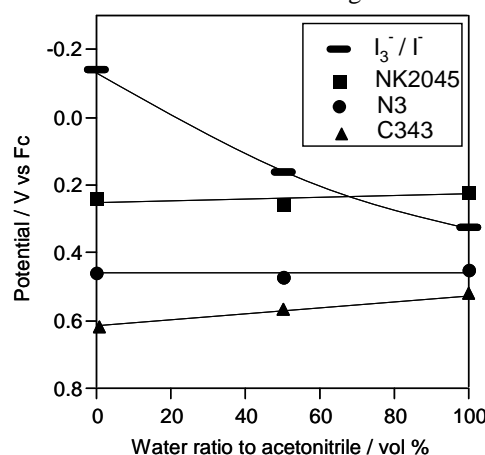


Fig. 3 Oxidation potentials (vs. Fc⁺/Fc) of dyes and I₃⁻/I⁻ redox couple in water-acetonitrile mixtures.

Reference

- [1] R. Abe et al. *Chem. Phys. Lett.*, **344**, 339 (2001)
- [2] K. Sayama et al. *Chem. Commun.*, 2416 (2001).